


**ZINC OXIDE, ITS PRODUCTION METHOD, AND TELLURITE GLASS FIBER AND OPTICAL AMPLIFICATION DEVICE USING THE ZINC OXIDE****Publication number:** JP2003192346 (A)**Also published as:****Publication date:** 2003-07-09 JP4022602 (B2)**Inventor(s):** KANO KOJI; MORI ATSUSHI; SHIMIZU MAKOTO; KOBAYASHI KENJI**Applicant(s):** NIPPON TELEGRAPH & TELEPHONE; NTT ELECTRONICS CORP**Classification:****- International:** G02B8/02; C01G9/02; C03C13/04; H01S3/06; H01S3/10; H01S3/17; G02B6/02; C01G9/00; C03C13/00; H01S3/06; H01S3/10; H01S3/17; (IPC1-7): C01G9/02; C03C13/04; G02B6/16; H01S3/06; H01S3/10; H01S3/17**- European:****Application number:** JP20010391388 20011225**Priority number(s):** JP20010391388 20011225**Abstract of JP 2003192346 (A)**

**PROBLEM TO BE SOLVED:** To provide a method for producing zinc oxide with high purity and a large particle diameter by overcoming a defect in the conventional production thereof such that its purity is low because a starting material is an aqueous solution including much impurities such as zinc salt or zincate, or the particle diameter is very small, a.g. 1 [μm] or less, and also provide an optical fiber using the zinc oxide and an optical amplification device composed by using the optical fiber.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of a zinc oxide with large particle diameter, and more particularly the manufacturing method of the zinc oxide of the high grade oxide material for light amplifiers by a high grade.

[0002]

[Description of the Prior Art]A zinc oxide (ZnO) is one of the tellurite glasses or composition raw materials of tellurite glass fiber which use as the main ingredients the tellurium dioxide ( $\text{TeO}_2$ ) which becomes a basis of an optical amplification medium, and the light amplifier and laser device which used this.

[0003]About the manufacturing method of the conventional zinc oxide, on the method and concrete target which get carbon dioxide in an operation of the saturated sodium bicarbonate solution in the solution of zincic acid, a sodium bicarbonate solution is added to the solution of the sulfate of zinc of zinc salt, and it calcinates and manufactures at an elevated temperature after producing zinc carbonate. In a conventional method, use the solution of zinc salt like sulfate of zinc, and the solution of zincic acid as a starting material, and in this solution still more specifically Namely, sodium carbonate, Or the solution of sodium bicarbonate is added, respectively, it calcinates at an elevated temperature after producing basic zinc carbonate and neutral zinc carbonate, and a zinc oxide is obtained.

[0004]About the manufacturing method of the conventional zinc oxide, the solution of zinc salt or zincic acid is used as a starting material. Since the zinc solution of the high grade was not being used for the solution of zinc salt or zincic acid, it had a fault from which the thing of a high grade is not obtained about the manufactured zinc oxide, either.

[0005]In a conventional method, in order to remain as an impurity into the zinc oxide which the trace of sulfuric acid of the used sulfate of zinc manufactured and to remove

this, it heats above 800 °C and there is complicatedness which must be used as the zinc oxide except the trace of sulfuric acid.

[0006]The zinc oxide manufactured by the manufacturing method of the conventional zinc oxide has very as fine-grained a feature as 1 micrometer or less. However, in tellurite glass production. A zinc oxide (ZnO), sodium oxide (Na<sub>2</sub>O), bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>), etc. which are the tellurium dioxide (TeO<sub>2</sub>) and accessory constituent of the main ingredients which are raw materials for glass are uniformly mixed with a mortar, and there is a process to heat.

[0007]When mixing was insufficient, there was a problem to which a zinc oxide remains from the difference in the specific gravity of these raw materials to a melting container bottom at the time of glass melting, and the presentation of the fused glass becomes uneven. That is, since the powdered particle diameter of the zinc oxide manufactured with the manufacturing method of the conventional zinc oxide was very fine, zinc oxides condensed in the shape of a ball by the mixing process, and since it was hard to distribute, obtaining a uniform mixed raw material had a fault which must continue prolonged mixing.

[0008]

[Problem(s) to be Solved by the Invention]The purpose of this invention by using the high-purity-metal zinc from which the impurity of transition metals, such as Fe, Cu, and nickel, was removed for a starting material, It is in the fault of the manufacture of a zinc oxide with low purity which uses solution with many impurities, such as zinc salt or zincic acid, as a starting material, and particle diameter providing 1 micrometer or less and the method of manufacturing a zinc oxide with large particle diameter by the high grade which solved the fault of manufacture of a very small zinc oxide.

[0009]

[Means for Solving the Problem]This invention is characterized by a manufacturing method of a zinc oxide comprising the following, in order to solve an aforementioned problem.

A process of using high purity zinc as a starting material, dissolving said high purity zinc in an acid solution, adding sodium hydroxide or a potassium hydrate to a zinc solution after the dissolution, and producing settlings of zinc hydroxide.

A process of washing these settlings while riping by heating and cooling in ultrapure water.

A process of drying and drying these settlings.

A process of forming a dried substance into a grinding narrow type.

[0010]Namely, after dissolving high-purity-metal zinc within acid solutions, such as chloride, nitric acid, and sulfuric acid, While riping these settlings by adding sodium

hydroxide or a potassium hydrate in solution after the dissolution, producing settlings of zinc hydroxide, heating these settlings in ultrapure water and cooling, After washing sodium ion or potassium ion and a chloride ion, nitrate ion, or sulfate ion, it dries and dries, a dried substance is formed into a grinding narrow type with a mortar, and it is considered as a zinc oxide with large particle diameter by a high grade.

[0011]In order that this invention may solve a problem of a method of adding sodium carbonate or a sodium bicarbonate solution to zincic acid of conventional technology, or solution of zinc salt, and manufacturing a zinc oxide from basic or neutral zinc carbonate, Purity with few transition metal impurities, such as Fe, nickel, and Cu, uses not less than 99.999% of high-purity-metal zinc for a starting material, by having the aging process of zinc hydroxide precipitation, it is a high grade with few transition metal impurities, and a zinc oxide with large particle diameter is manufactured.

[0012]

[Embodiment of the Invention]The zinc of a high grade is useful on a use among the metal zinc used as a starting material in this invention. As for the grade of a high grade, not less than 99.999% (i.e., more than 5N) is preferred. It is not restricted to the shape of metal zinc. That is, powder, the shape of an ingot, and the shape of a shot-like throat may be sufficient.

[0013]In this invention, the above high purity zinc is dissolved with acid. What is necessary is just the conditions which do not need special conditions for the dissolution by acid, but can be dissolved into solutions, such as chloride, nitric acid, and sulfuric acid, in this metal zinc.

[0014]Special conditions are not needed about the heating and dissolving of the solution which dissolved this metal zinc. Although chloride, nitric acid, sulfuric acid, etc. can be used as mentioned above as said acid, not less than 99.99% of the purity is desirable in order to manufacture a high grade zinc oxide.

[0015]Next, it settles [ add sodium hydroxide or a potassium hydrate to this zinc solution, and ] zinc hydroxide and dries [ ripe, wash and ]. In order for such sodium hydroxide or a potassium hydrate to also manufacture a high grade zinc oxide, it is preferred that purity is not less than 99.99%.

[0016]Here, by aging meaning enlarging the crystal size of precipitate and repeating heating cooling as mentioned above, a small crystal is dissolved and a big crystal is re-deposited. Therefore, the process of riping by heating and cooling and washing these settlings in ultrapure water may be a singular number time, and can also be repeated two or more times.

[0017]What is necessary is just to perform heating and washing, while aging of zinc hydroxide and washing operation also add and agitate ultrapure water, and the method in ordinary use may be used also for drying, and centrifugal separation is preferred for it operationally. The method of desiccation and the daily use also about grinding may be

used, and vacuum drying and grinding by the mortar made from Teflon (registered trademark) are suitable for the last operationally.

[0018]As mentioned above, as explained concretely, in the case of the method of manufacturing especially the zinc oxide of a high grade, in this invention method. The method of using the zinc salt or zincic acid of conventional technology as a starting material, dissolving in acid, adding sodium carbonate or sodium bicarbonate, considering it as carbonate, calcinating this at an elevated temperature, and using as a zinc oxide, High-purity-metal zinc is used as a starting material, and it differs in that sodium hydroxide or the potassium hydrate of a point and a high grade which dissolves in acid of a high grade is added.

[0019]Tellurite glass fiber is producible using the zinc oxide obtained by this invention. In the production, as ZnO of this invention,  $\text{TeO}_2$  of the main ingredients, and other accessory constituents, For example, the raw material containing  $\text{Na}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  is prepared, The process of producing the melt of the core glass fused under oxygen environment, and clad glass, The publicly known method of using can apply the process of carrying out suction shaping (suction casting) of these melts, and producing preforming, and the process of drawing a line in a fiber from preforming (for example, JP,11-236240,A). Addition of  $\text{Bi}_2\text{O}_3$  has a function which raises the refractive index of glass, and the rate of specific refraction between core clads is controlled by the addition.

[0020]If rare earth, such as Er, Pr, Yb, Nd, Ce, Sm, Tm, Eu, Tb, Ho, or Dy, is added on the aforementioned core or clad glass of tellurite glass fiber, the tellurite glass fiber in which the amplifying function was given can be obtained. By making into a constitutional unit tellurite glass fiber in which these rare earth was added, if publicly known constructing technique is applied, various kinds of light amplifier as shown in drawing 4 is realizable (for example, JP,11-236240,A etc.).

[0021]Here, drawing 4 (A) is a light amplifier, the signal light source 1 and the excitation light source 2 are connected to one end of the rare earth addition tellurite glass fiber 4 via the optical coupler 3, and the optical isolator 5 is connected to the other end of the rare earth addition tellurite glass fiber 4. The function of a light amplifier amplifies an optical signal in the rare earth addition tellurite glass fiber 4, and outputs it from the output optical fiber 6d.

[0022]6a-6c are the fibers and the fibers for [ 6 d ] an output which connect each part article. Drawing 4 (B) is a laser device, instead of the signal light source 1, it connects the output side of the optical isolator 5 to the optical coupler 3, forms the optical resonator of ring shape, and inserts the narrow band pass filters 7 in the middle of this ring shape optical resonator. In the penetration region of the narrow band pass filters 7, the function of a laser device carries out laser oscillation among the lights amplified with

the rare earth addition tellurite glass fiber 4.

[0023]It is reflected by the reflector 8, and the spontaneous emission light (ASE) generated in the rare earth addition tellurite glass fiber which shows an ASE light source device and is shown by 4 passes through the inside of the rare earth addition tellurite glass fiber 4 again, and is amplified, and drawing 4 (C) is emitted from 6d of ends of the optical coupler 3, and is a thing. an ASE light source device -- extensive -- it functions as a wavelength band light source.

[0024]

[Example]Hereafter, although an example explains this invention still more concretely, this invention is not limited to these examples.

[0025]

[Example 1] Purity: Shape carries out weighing of the shot-like high-purity-metal zinc 25g by 7N (99.99999%), put into a 1000-ml beaker, and add 500 ml of ultrapure water. Zinc is dissolved adding nitric acid of the high grade for electronic industry to this, and heating. In this case, although divided and added, taking care that nitric acid does not become superfluous, zinc dissolved the addition thoroughly at a total of 75 ml.

[0026]Commercial super-high-purity 3M sodium hydroxide solution is added little by little to this solution, and zinc hydroxide precipitation is obtained. In this case, when sodium hydroxide was superfluous, in order that settlings might remelt, the quantity of the sodium hydroxide to add was 260 ml which becomes zinc with the equivalent mostly. A centrifuge separates these settlings into settlings and solution.

[0027]The settlings after separation perform aging and washing again by putting into a 1000-ml beaker, and 500 ml's adding, and heating and agitating ultrapure water. A centrifuge separates into settlings and solution after cooling. Aging and washing operation are repeated 3 times. After washing, zinc hydroxide dries by a vacuum dryer, is ground and narrow-type-ized with the mortar made from Teflon (registered trademark), and let it be a zinc oxide.

[0028]The reaction formula can manufacture a zinc oxide according to the formula 1, the formula 2, and the formula 3.

[0029]Formula 1  $Zn + 2HNO_3 \rightarrow Zn^{2+} + 2NO_3^- + H_2^{**}$  [0030]Formula 2  $Zn^{2+} + 2NaOH \rightarrow Zn$

$(OH)_2^{**} + 2Na^+$  [0031]Formula 3  $Zn(OH)_2 \rightarrow ZnO + H_2O^{**}$  [0032]Drawing 1 (A) is an X diffraction figure of the zinc oxide after vacuum drying and mortar grinding. In a figure, a horizontal axis is the angle of diffraction 2 theta (deg), and a vertical axis is the diffraction intensity of X-rays. Drawing 1 (B) is a profile of JCPDS card No.36-1451 (ZnO).

[0033]In the figure, a horizontal axis is the angle of diffraction 2 theta (deg), a vertical axis is the relative intensity of X-rays, the number in a parenthesis is a Miller index, and the peak whose relative intensity is comparatively large is shown. Drawing 1 (A) of the

relative value of a peak position and X-ray intensity corresponds with drawing 1 (B) well, and it turns out that the substance obtained by this invention is a zinc oxide.

[0034]The substance produced by this invention is heated in argon gas from a room temperature to 1000 \*\*, Since there is also no weight change and quantity-of-heat change as a result of observing by the thermometric analysis (TG-DTA) which measures a weight change and quantity-of-heat change, in accordance with the result of said X diffraction, it can be said that the substance obtained by this invention is a zinc oxide.

[0035]Conduct activation analysis of Fe of the produced zinc oxide, nickel, and Cu, and Fe, Each element has produced the anhydrous zinc oxide of the high grade of triple or more figures about nickel and Cu rather than the fixed-quantity value of the impurity concentration of Fe about the zinc oxide in which an analysis result of 1 ppb or less was obtained, and impurity concentration was manufactured conventionally, nickel, and Cu.

[0036]Drawing 2 is the result of observing with an electron microscope about the particle diameter of the zinc oxide obtained by this invention. Drawing 2 (A) is a 10000 time electron microscope photograph, and drawing 2 (B) is a 25000 time electron microscope photograph. The electron microscope photograph of a commercial zinc oxide with comparatively high purity is also shown as drawing 3 for comparison. Drawing 3 (A) is a 15000 time electron microscope photograph, and drawing 3 (B) is a 40000 time electron microscope photograph.

[0037]a commercial zinc oxide -- a size -- 0.5 micrometer or less -- shape -- until [ from tabular ] granular -- it is various and signs that particles are condensing are known. On the other hand, as for the zinc oxide manufactured by this invention, it turns out that length is a uniform crystal with as cylindrical 1 micrometer and thickness as about 0.2 micrometer. The yield of the zinc oxide with large particle diameter was 90% in the high grade in this example.

[0038]

[Example 2] Use as an accessory constituent the zinc oxide (ZnO) produced by this invention, and  $\text{Na}_2\text{O}$  of the accessory constituent of the tellurium dioxide ( $\text{TeO}_2$ ) of the main ingredients and others, [ this ] the tellurite glass fiber (core glass presentation: --  $\text{TeO}_2$ -ZnO- $\text{Na}_2\text{O}$ - $\text{Bi}_2\text{O}_3$  --) which added  $\text{Bi}_2\text{O}_3$  [ 3 and ] Clad glass composition: The single mode fiber of  $\text{TeO}_2$ -ZnO- $\text{Na}_2\text{O}$  was produced. The time which mixing by the mortar in a dry box took these oxides in front of glass melting is 30 minutes, and was shortened by 4 by about 1/compared with the case where ZnO of the conventional marketing is used.

[0039]As a result of wavelength's measuring the loss at 1.3 micrometers about the fiber produced from compound glass, it turned out that a fiber of 10dB/km is obtained. Since the tellurite glass fiber of elegance used the commercial ZnO raw material

conventionally, this has attained reduction of the large loss value to the loss value at 1.3 micrometers having shown the value high in km and 1000dB /.

[0040]

[Effect of the Invention]As mentioned above, as explained in detail, according to the manufacturing method of this invention, the metal zinc of a high grade is used as a starting material, Sodium hydroxide or a potassium hydrate is added after dissolving in acid of a high grade, and the zinc oxide whose particle diameter is a cylindrical crystal of 1 micrometers or more can be manufactured by an anhydrous high grade after producing the settlings of zinc hydroxide by aging by heating in ultrapure water, washing, subsequent drying, desiccation, and grinding.

[0041]It compares with the method of obtaining carbon dioxide in an operation of the saturated sodium bicarbonate solution or a sodium carbonate solution in conventional zincic acid or the solution of zinc salt especially, Since a zinc oxide with large particle diameter is produced by anhydrous very simple, the high grade zinc oxide which made the transition metal super-low concentration can be manufactured. Low-loss tellurite glass fiber can be manufactured by using a zinc oxide as a starting material of tellurite glass fiber. There is an advantage which can manufacture light amplifier with high amplification by furthermore using this tellurite glass fiber.

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## CLAIMS

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[Claim(s)]

[Claim 1]A manufacturing method of a zinc oxide characterized by comprising the following.

A process of using high purity zinc as a starting material, dissolving said high purity zinc in an acid solution, adding sodium hydroxide or a potassium hydrate to a zinc solution after the dissolution, and producing settlings of zinc hydroxide.

A process of washing these settlings while riping by heating and cooling in ultrapure water.

A process of drying and drying these settlings.

A process of forming a dried substance into a grinding narrow type.

[Claim 2]A manufacturing method of the zinc oxide according to claim 1 in which high purity zinc is high purity metal of not less than 99.999% of purity, purity is not less than 99.99% of high grade reagent, and sodium hydroxide and a potassium hydrate are also characterized by purity being a reagent of not less than 99.99% of high grade also about acid.

[Claim 3]Claim 1 repeating a process of washing these settlings while riping by heating and cooling in ultrapure water, two or more times, or a manufacturing method of a zinc oxide of two given in any 1 paragraph.

[Claim 4]A zinc oxide manufacturing by the manufacturing method according to claim 1 to 3.

[Claim 5]Tellurite glass fiber containing the zinc oxide according to claim 4.

[Claim 6]Light amplifier using the tellurite glass fiber according to claim 5.

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